FORMATION AND NATURE OF NITROGENOUS GUM DERIVED FROM COKE-OVEN GAS UNDER CRYOGENIC CONDITIONS

by
W. Kulak
E. V. Nagle
J. G. Crist

Applied Research Laboratory
United States Steel Corporation
Monroeville, Pennsylvania

Introduction

A type of nitrogenous gum called "vapor-phase gum" has long been known to form in coke-oven gas. It is generally accepted that the formation of this gum is due primarily to the interaction of nitric oxide (NO), oxygen, and organic compounds such as the unsaturated hydrocarbons. Another type of nitrogenous gum is one that is formed in coke-oven gas under cryogenic conditions that also involves the interaction of nitric oxide, oxygen, and hydrocarbons. It is widely recognized[1,2,3,4]* that NO by itself does not react with gum-forming hydrocarbons; however, under cryogenic conditions the oxidation of NO or its dimer, $(NO)_2$, is rapid and the products of the oxidation, nitrogen trioxide (N_2O_3) and nitrogen tetroxide (N_2O_4), react with gum-forming hydrocarbons. In the liquid phase, ethylene is known to react with N_2O_3 and N_2O_4; however, such reactions are slow at low temperatures.[1,5] Generally it is assumed that nitrogen oxides react primarily with cyclopentadiene and butadiene when present in liquid ethylene. It is the purpose of this paper to present the results of work undertaken to investigate the reactions, and the products of the reactions, of N_2O_3 and N_2O_4 with cyclopentadiene and butadiene in liquid ethylene. For comparison, some investigations were made in which liquid ethane was used in place of liquid ethylene.

Materials and Experimental Work

Materials - All materials were obtained from The Matheson Company. Ethylene (99.5% minimum purity) and ethane (99.0% minimum) were purified by passage through activated carbon. Butadiene and N_2O_3 (both 99.0% minimum purity) and N_2O_4 (99.5% minimum) were used as received. Cyclopentadiene was freshly distilled as needed; mass-spectrometric analysis of the distilled material showed it to contain 93.8 percent cyclopentadiene, 2.7 percent dicyclopentadiene, 2.9 percent 1,3-cyclohexadiene, 0.5 percent benzene, and less than 0.1 percent toluene.

Apparatus and Procedure - Liquid ethylene (or ethane) for the tests was prepared by passing the Matheson gas through activated

---

* See References.

carbon and condensing it at atmospheric pressure and, as well as possible, in the absence of air. As the first step in preparing the gums, the Pyrex condenser and receiver were purged with gaseous ethylene (or ethane) and the receiver was cooled with liquid nitrogen. When cyclopentadiene was used, a weighed amount of the diene was injected into the receiver through a septum-covered port by means of a syringe and about 200 cubic centimeters (cc) of liquid ethylene (or ethane) were then condensed into the receiver. When butadiene was used, it was more convenient to condense the liquid ethylene (or ethane) into the receiver first and then inject a measured volume of butadiene gas into the liquid by means of a graduated syringe. With either procedure, the next step was to introduce a measured volume of N_2O_3 or N_2O_4 into the liquid with a graduated syringe. The following procedure was followed to minimize the amount of nitrogen oxide that escaped as vapor during this operation. The syringe tip (a polyethylene tube) was inserted into the liquid and a small portion of liquid was withdrawn into the partially filled syringe containing nitrogen oxide; this liquid vaporized and expelled the nitrogen oxide from the syringe. The operation was repeated several times to ensure that all of the nitrogen oxide was flushed into the receiver. (With ethylene, the temperature of the reaction mixture was about -105 C; with ethane, the temperature of the reaction mixture was about -90 C.) After 15 minutes in the receiver, the mixture was placed in a loosely covered vessel and left to stand until the liquid evaporated (about 1 hour).

For colorimetric examinations, the gums remaining after evaporation of the reaction mixtures were weighed and then dissolved in 20 milliliters (ml) of a 1 percent aqueous solution of sodium hydroxide. The solutions were allowed to stand 20 to 30 minutes for color development, and the spectral absorbance was then measured at a wavelength of 425 millimicrons on a Beckman Model DU spectrophotometer. With some solutions, the optical densities were too high to be measured and dilution with known amounts of additional caustic was necessary.

For infrared measurement, the gum residue was mounted on a sodium chloride plate immediately after it was isolated, and its spectrum from 2 to 15 microns was obtained. Infrared measurements were also repeated after the gum residues had been stored for varying numbers of days on the plates.

For determination of the nitrogen content of a gum residue, the gum was first allowed to stand overnight. On the following day, the weight of the gum was determined and the gum was dissolved by adding dilute (1%) aqueous sodium hydroxide to the vessel. The gum in the caustic solution was then reduced with Devarda's metal and subsequently analyzed for nitrogen by the Kjeldahl method.

Results and Discussion

Gums were formed rapidly when N_2O_3 and either butadiene or cyclopentadiene were introduced into liquid ethylene; however, the

yields of gum varied considerably with differences in the mole ratio of N_2O_3 to butadiene. In fact, difficulties were encountered in reproducing the yield of gum with any particular mole ratio of reactants. Variations were most noticeable with the reaction mixtures prepared with butadiene. Because of such variations, the reaction mixtures in which this compound had been introduced were divided into aliquots so that multiple determinations of the gum content could be made. The variability in the yield of gum might be explained if the initial products formed from the reactants can either evaporate or polymerize into the non-volatile gum.

In an attempt to develop a method for quantitative determination of the gums, aqueous sodium hydroxide solutions of gums were prepared and examined spectrophotometrically. The absorbance of light of 425-millimicron wavelength (selected from an examination of the absorption spectra of such solutions) was found to be roughly proportional to the concentration of the gum, Figure 1. As the ratio of nitrogen oxide to diene was increased, however, the slopes of the Beer's law plots shifted markedly and irregularly, Figures 1 and 2. The technique therefore could not be used to estimate gum concentrations.

Significantly more gum was obtained from cyclopentadiene than from butadiene. For example, at a ratio of about 0.75 moles of N_2O_3 per mole of diene (in liquid ethylene) cyclopentadiene yielded about 0.5 grams of gum per gram of diene whereas butadiene yielded only about 0.1 grams. One possible reason for this difference may be that the products of the reaction with cyclopentadiene are less volatile and tend to remain as residue upon evaporation of the ethylene.

As shown in Figure 3, air appeared to retard the gum formation when N_2O_3 and cyclopentadiene were introduced into liquid ethylene, since greater yields of gum were obtained when air was excluded from the reaction mixtures. It may be that air oxidizes the N_2O_3 to N_2O_4, which is less reactive as a gum former.

Participation of Ethylene in Gum Formation

Under the conditions of the described tests, no gums were formed when only N_2O_3 was added to liquid ethylene. Nevertheless, ethylene was found to take part in the gum formation when both N_2O_3 and cyclopentadiene were introduced into liquid ethylene.

When the amount of N_2O_3 charged was in considerable excess of the amount of cyclopentadiene, the yield of gum was considerably greater than the amount of cyclopentadiene charged, Figure 4. The nitrogen content of such gums was only 6.7 to 7.8 percent, however, indicating that N_2O_3 did not comprise the major portion of the gum. It was therefore apparent that the gum contained ethylene, and because of the participation of ethylene, the yields of gum were not limited by the amounts of dienes available.

Because ethane was not expected to react with the gum-formers

at the temperatures employed (about -100 C), several tests were made in which the nitrogen oxide and diene were mixed with liquid ethane instead of liquid ethylene. Comparison of the results of these tests with the results obtained with ethylene gave further evidence that ethylene participated in gum formation.

Plots of the yields of gum per gram of cyclopentadiene charged against the starting reactant ratios are shown in Figure 5. In liquid ethane, the highest yield of gum per gram of cyclopentadiene was obtained when near equimolecular amounts of N_2O_3 and cyclopentadiene were used, and in contrast to the results obtained with liquid ethylene, the yield of gum per gram of cyclopentadiene subsequently decreased as the proportion of cyclopentadiene charged was decreased. Thus, the divergence of the curves for the gum yields per gram of cyclopentadiene in the two liquids indicates that ethylene was incorporated in the gum. As illustrated by the curves presented in Figure 6, the gum yields per gram of N_2O_3 charged also appeared to differ somewhat in the two media.

Gum Formation From the Addition of N_2O_4 and Cyclopentadiene to Liquid Ethylene

Gums were also formed when N_2O_4 and cyclopentadiene were added to liquid ethylene, Figure 7. The gum-forming reaction was similar to that obtained with N_2O_3 in that gum of about the same nitrogen content was produced and at least some and probably all, of the gums contained ethylene; however, the gum yields were somewhat smaller.

The gum produced from N_2O_4 and cyclopentadiene in ethylene contained 5.8 to 7.1 weight percent nitrogen, which was about the same as for the gums produced from N_2O_3 and cyclopentadiene in ethylene (6.7 to 7.8 wt %). That the gum formed from N_2O_4 contained ethylene was evident from the fact that the yields of gum at the higher N_2O_4-to-cyclopentadiene ratios tested were unusually high for the amounts of cyclopentadiene charged and, as shown by the nitrogen content of the gums, these unusually high yields could not be accounted for by the proportion of N_2O_4 incorporated in the gum. Regardless of the ratios of N_2O_4 to cyclopentadiene, the gums all contained about the same percentage of nitrogen.

The gum yields with N_2O_4 were somewhat less than with N_2O_3, as indicated by experiments in which gums were produced with the two nitrogen oxides by procedures made as identical as possible. By starting with 1.5 moles of the nitrogen oxide per mole of cyclopentadiene, the yield of gum per gram of cyclopentadiene was about 1.5 grams with N_2O_3 and about 1.2 grams with N_2O_4.

Infrared Examination of Gums

Infrared spectra were obtained for 13 samples of gum produced

by mixing cyclopentadiene and N_2O_3 with liquid ethylene. That the spectra are those of a highly unstable gum was confirmed when one of the freshly isolated samples "fumed-off" after it was placed on a sodium chloride plate for infrared examination. Typical spectra are shown in Figures 8, 9, and 10 for gums produced from N_2O_3-to-cyclopentadiene mole ratios of 0.52, 2.3, and 7.7, respectively.

In the spectra of the gum, characteristic absorptions were noted for several groups of atoms. Evidence of the following groups was obtained in all gum samples:

(1) -OH or -NH (possibly representing hydrogen bonding).
(2) -CH (merely indicating carbon-hydrogen linkages in general).
(3) C=O (shifted in concentration and structure during storage of samples).
(4) $-ONO_2$ (definitely organic nitrate).
(5) $-CNO_2$ (organic nitro groups).
(6) $NaNO_3$.

The same identifications were also made in samples prepared by passing N_2O_3 through cyclopentadiene in the absence of ethylene; however, the residue from the evaporation of ethylene treated with N_2O_3 in the absence of cyclopentadiene showed only the $NaNO_3$ absorption. $NaNO_3$ is probably present in all of the samples because of a reaction of nitrogen oxides with the salt plate in the presence of moisture.

The functional groups whose presence was detected (carbonyl, nitro, and nitrate) or suspected (hydroxyl) in the gum were among those found by Levy and co-workers[5] in the products of the reaction of N_2O_3 and N_2O_4 with simple olefins at 0 C. According to Levy, when N_2O_3 and an unsaturated compound are reacted, the primary reaction is a simple addition to yield products (usually several) containing nitro ($-NO_2$), nitrite (-ONO), and nitroso (-NO) groups. Products containing nitrite and nitroso groups are seldom isolated, apparently because of their instability (if isolated from solution they usually explode) and ensuing secondary reactions. Nitrite groups are frequently oxidized by N_2O_4 to nitrate groups; however, they may also be hydrolyzed (for example, by water produced by oxidation) to produce hydroxyl groups and nitric or nitrous acid. The fate of nitroso groups is not known. Carbonyl groups might be expected to result from the nitrogen oxide oxidation of carbons having nitro groups.

* * *

In summary, the experimental investigations have confirmed that nitrogenous gums are formed when N_2O_3 or N_2O_4 and cyclopentadiene or butadiene are introduced into liquid ethylene. Indications were obtained that ethylene is readily incorporated in the gum. Some of the reaction products are apparently volatile; however, other material formed remains as a gummy residue when the solvent ethylene is evaporated. Whereas the yields of gum per unit weight of diene increase

with an increase in the ratio of N_2O_3 to diene, the nitrogen content of the gum prepared from N_2O_3 and cyclopentadiene in ethylene was 5.8 to 7.1 weight percent, regardless of the starting reactant ratio. Furthermore, the yields were not limited by the amount of diene present but only by the amount of nitrogen oxide available. The yields of gum residue were greater with cyclopentadiene than with butadiene and the yields appeared to be favored by the absence of air. It may be that air oxidizes N_2O_3 to N_2O_4, which is less reactive as a gum former. Infrared studies have shown what functional groups are present in the gum, and the spectra obtained should be useful as references in examining materials formed under similar conditions.

Acknowledgement

The authors wish to acknowledge the assistance of A. J. Miskalis, who measured and interpreted the infrared spectra of the gum samples, R. W. Baudoux, who determined their nitrogen content, and Dr. M. H. Wilt, for helpful suggestions during the work and for reviewing the manuscript.

References

1. F. Rottmayr, Linde Berichte aus Tecknik und Wissenschaft, No. 7 (1959).

2. N. V. Sidgwick, The Organic Chemistry of Nitrogen, Clarendon Press, Oxford, 1949, p. 213.

3. J. F. Brown, Jr., J. Am. Chem. Soc., 79, 2480 (1957).

4. Whytelaw-Gray, Gas Journal, November 11, 1936, p. 465.

5. N. Levy, et al., J. Chem. Soc. (London), 1946, 1093-1104.

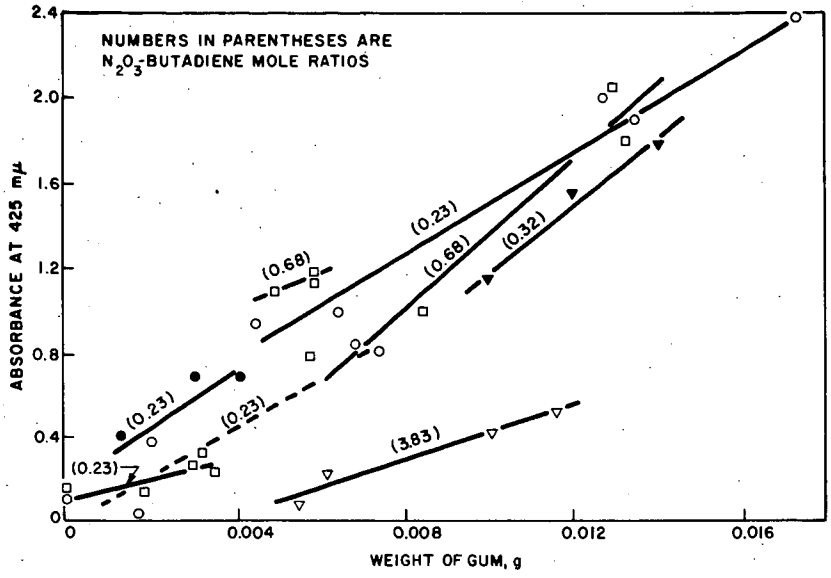

Fig. 1.-SPECTRAL ABSORBENCE OF CAUSTIC SOLUTIONS OF GUMS PREPARED FROM NITROGEN TRIOXIDE AND BUTADIENE IN LIQUID ETHYLENE

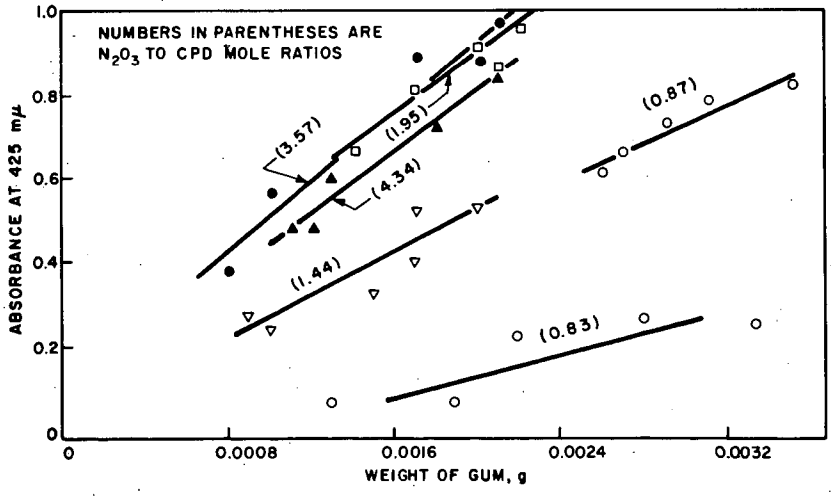

Fig. 2.-SPECTRAL ABSORBENCE OF CAUSTIC SOLUTIONS OF GUMS PREPARED FROM CYCLOPENTADIENE AND N_2O_3 IN ETHYLENE

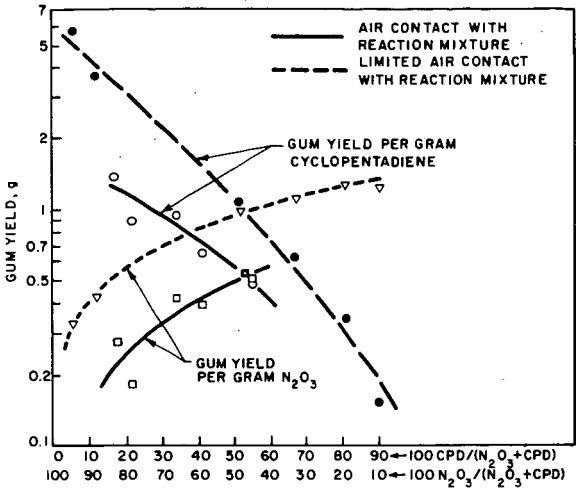

Fig. 3.-YIELDS OF GUM FROM DIFFERENT N_2O_3 TO CYCLOPENTADIENE RATIOS (IN LIQUID ETHYLENE)

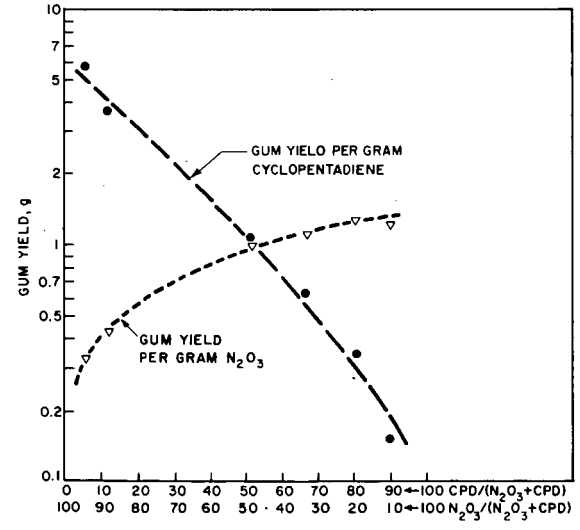

Fig. 4.-YIELDS OF GUM FROM DIFFERENT N_2O_3 TO CYCLOPENTADIENE RATIOS (IN LIQUID ETHYLENE)

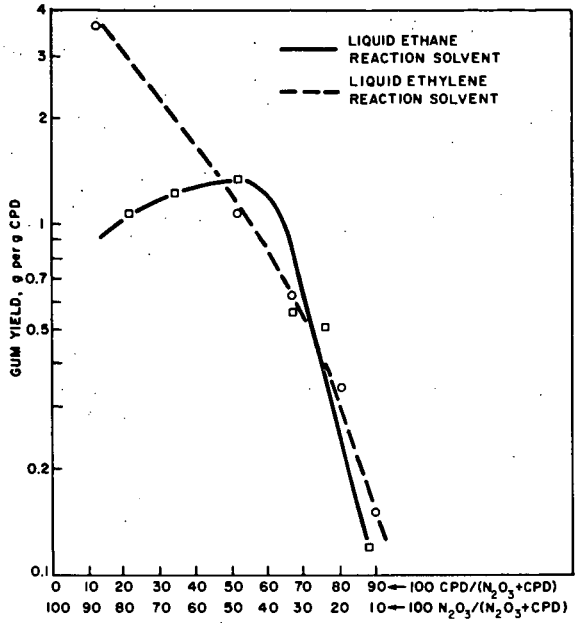

Fig. 5.-YIELDS OF GUM FROM DIFFERENT N_2O_3 TO CYCLOPENTADIENE RATIOS

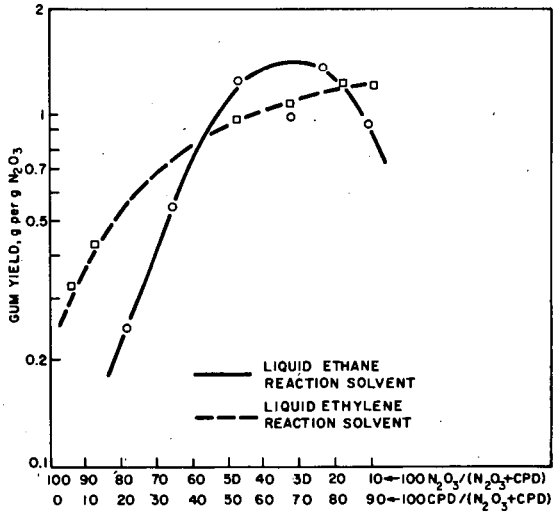

Fig. 6.-YIELDS OF GUM FROM DIFFERENT N_2O_3 TO CYCLOPENTADIENE RATIOS

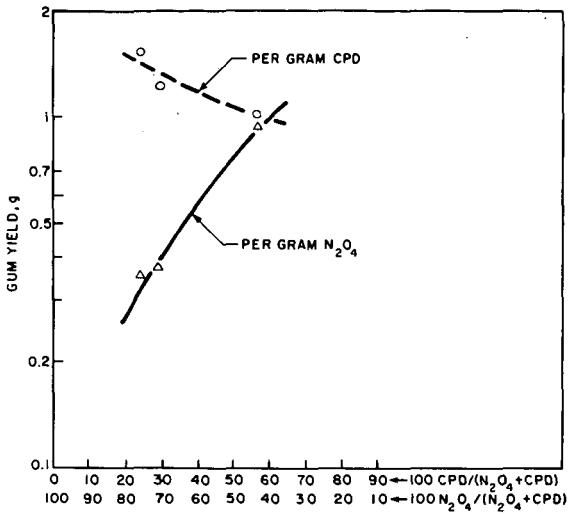

Fig. 7.-YIELDS OF GUM FROM DIFFERENT N_2O_4 TO CYCLOPENTADIENE RATIOS

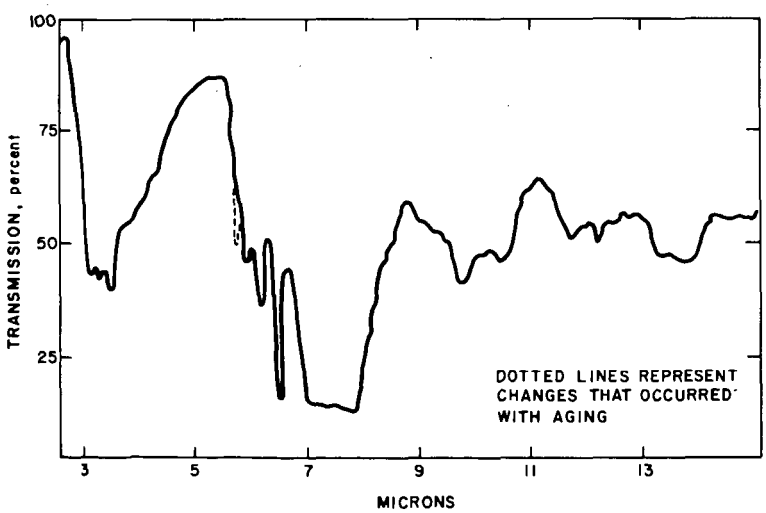

Fig. 8.-INFRARED SPECTRUM OF GUM PRODUCED FROM THE REACTION OF N_2O_3 AND CYCLOPENTADIENE IN ETHYLENE (0.52 MOLE N_2O_3 PER MOLE OF CYCLOPENTADIENE)

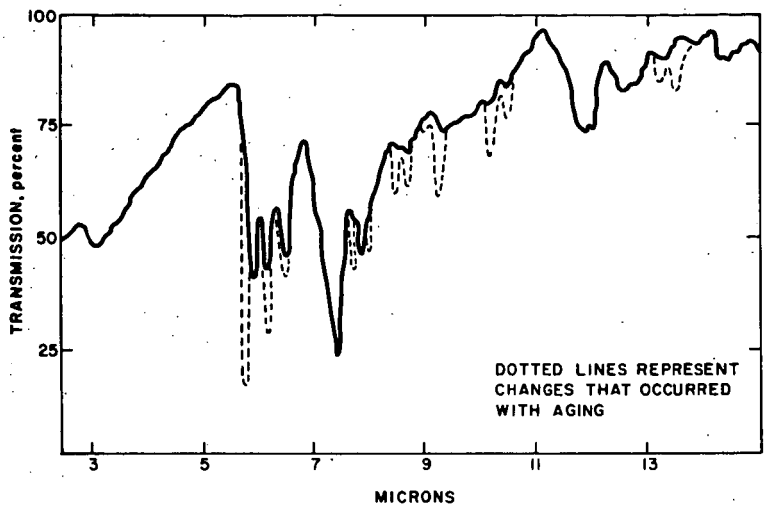

Fig. 9.-INFRARED SPECTRUM OF GUM PRODUCED FROM THE REACTION OF N_2O_3 AND CYCLOPENTADIENE IN ETHYLENE (2.30 MOLES N_2O_3 PER MOLE OF CYCLOPENTADIENE)

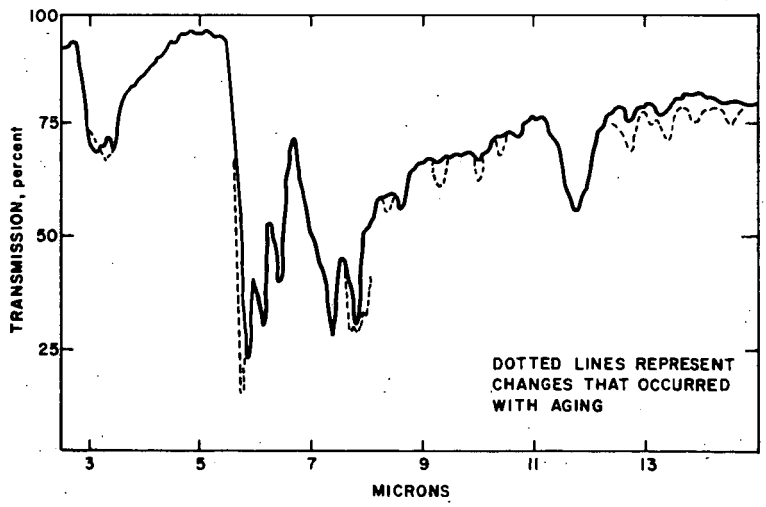

Fig. 10.-INFRARED SPECTRUM OF GUM PRODUCED FROM THE REACTION OF N_2O_3 AND CYCLOPENTADIENE IN ETHYLENE (7.73 MOLES N_2O_3 PER MOLE OF CYCLOPENTADIENE)